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RADIATION EFFECTS ON HIGH PERFORMANCE POLYMERS

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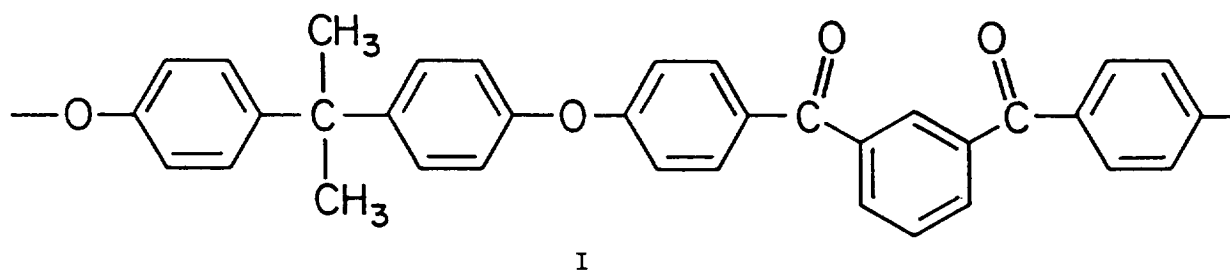
## RADIATION EFFECTS ON HIGH PERFORMANCE POLYMERS [1,2]

### INTRODUCTION

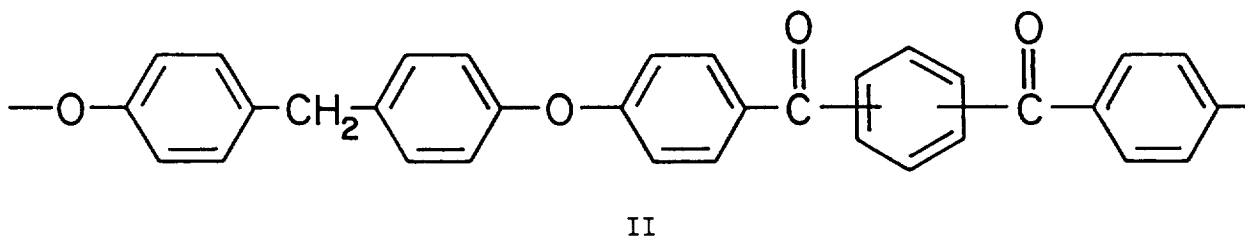
Polymer matrix materials are candidates for use in large space antennas and space platforms that may be deployed in geosynchronous orbit 22,500 miles above the earth. A principal concern are the long-term (e.g.,  $\geq 25$  years) effects of an environment that is hostile to organic polymers, including high-energy electromagnetic radiation, bombardment by charged particles, and large abrupt changes in temperature. In this study two polyarylene ethers which might be utilized as models for polymers in space applications were subjected to dosages of 70 keV electrons up to  $3.4 \times 10^{10}$  rad. The irradiated films were then examined to determine the effects of the high-energy electrons.

### EXPERIMENTAL

The principal object of study in this research is the product of a condensation reaction of bisphenol A with 1,3-bis(4-chlorobenzoyl)benzene [3]. It is designated Polymer I:



It is an amorphous material with  $\bar{M}_n = 2.9 \times 10^4$  g mol<sup>-1</sup> and  $T_g = 153^\circ\text{C}$ . The other polyether in this study, Polymer II, a slightly crystalline material, was prepared by reacting bis(4-hydroxyphenyl)methane and a 3:1 mixture of the meta and para isomers of bis(4-chlorobenzoyl)benzene [3]:



Films, 1-2 mil thick, were prepared from solutions in DMAc (Polymer I) or 1,1,2,2,-tetrachloroethane (Polymer II). They were irradiated at room temperature in a stainless steel vacuum ( $10^{-7}$  torr) chamber at a rate of

$4.5 \times 10^{-8}$  amp  $\text{cm}^{-2}$  as determined with Faraday cups. This corresponds to  $1.8 \times 10^8$  rad  $\text{hr}^{-1}$ . The source was a Kimball Physics Inc. electron gun.

After irradiation, the films were placed in a measured quantity of chloroform. Any gel present was separated by filtration from the resulting solution. Intrinsic viscosities of the solutions of the soluble fraction were measured in chloroform. Also, NMR (Varian FT-80A) spectra were obtained from solutions of Polymer I dissolved in deuteriochloroform.

During this study a new irradiation facility was finished. It has a mass spectrometer positioned between the sample and the vacuum pump so that volatile products can be monitored as they are formed during irradiation. The instrument, however, was not fully functional by the end of this study and data acquired with it are judged to be not reliable enough to report.

## RESULTS

Films of Polymer I and II were bombarded with high-energy electrons for up to 200 hours. No change in mass was detected after irradiation. The relative amounts of the soluble fractions of the two polyethers are shown in Figures 1 and 2 as a function of the length of time the films were irradiated. A gel component in films of Polymer I appeared near  $1.1 \times 10^{10}$  rad and by ca.  $2.9 \times 10^{10}$  rad 80% of the film had become crosslinked gel. Polymer II, on the other hand, began to crosslink almost at the onset of radiation. By  $1.8 \times 10^{10}$  rad it was 90% gel.

Samples of Polymer I, after being subjected to various doses, were mixed with chloroform and injected into a gel permeation chromatograph. The ratio of the mass of irradiated film to the volume of chloroform was the same for all samples. The GPC detector responses for the samples are superimposed in Figure 3. Relative amounts of sol in each sample were determined from the areas under the curves and have been included in Figure 1. The GPC results on 20-hr and 45-hr films show an increase in the high molecular-weight end of the distribution while the maximum in the distribution appeared at longer retention volumes as the duration of irradiation increased.

The intrinsic viscosities  $[\eta]$  for chloroform solutions of sol fractions of Polymer I and II have been plotted in Figure 4. For Polymer I  $[\eta]$  increased slowly with dosage to ca.  $1.4 \times 10^{10}$  rad, at which point it declined rapidly. The viscosity of solutions with Polymer II showed different behavior, declining monotonically with dosage from the start of the irradiation.

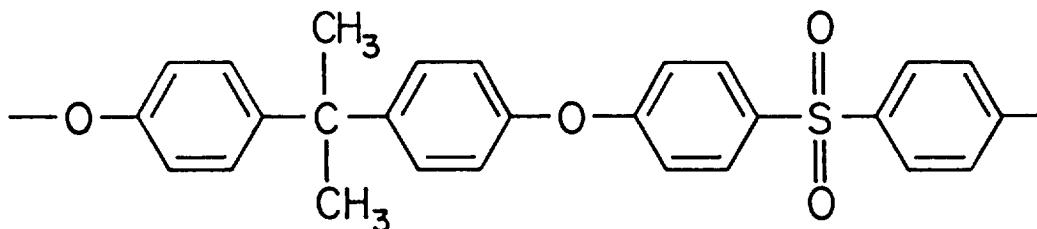
The integrated NMR spectra of soluble samples of Polymer I show that the ratio of phenyl hydrogens to alkyl hydrogens in irradiated samples compared to the same ratio in an unirradiated sample increases by 2.9, 3.3, and 4.0% for irradiation doses of  $0.4 \times 10^{10}$ ,  $1.6 \times 10^{10}$  and  $2.2 \times 10^{10}$  rad, respectively. Qualitatively, the NMR spectrum of the aromatic hydrogens in I changes little with irradiation; however, small peaks at 0.9 and 1.3 ppm.

(relative to TMS), that were not present before irradiation, appear adjacent to the methyl peak at 1.7 ppm.

Infrared absorbance measurements by Kiefer [4] on the same samples of Polymer I showed a diminution in the intensity of peaks associated with phenyl-carbonyl and phenyl-ether groups with increasing dose of electrons. In addition a small decrease in an absorption peak at  $2968\text{ cm}^{-1}$  indicates the loss of methyl hydrogens. There is no evidence of hydroxyl formation.

## DISCUSSION

The evidence presented indicates that electron bombardment of Polymer I and II causes both chain scission and crosslinking. An estimate of the number of crosslinkages  $G(X)$  and chain-scissions  $G(S)$  per 100 eV absorbed can be obtained from a Charlesby-Pinner [5] plot of  $S + S^{1/2}$  vs.  $1/R$ , where  $S$  is the fraction of film remaining soluble after a radiation dose  $R$ . (See Figure 5.) For Polymer I,  $G_I(X)$  is between  $1.0 \times 10^{-3}$  and  $1.5 \times 10^{-3}$  and  $G_I(S)$  is in the range  $0.2 \times 10^{-3}$  and  $0.8 \times 10^{-3}$ . Based on the assumption  $2 < \bar{M}_n \times 10^{-4} < 3$  for Polymer II, we estimate  $G_{II}(X)$  to be between  $4 \times 10^{-3}$  and  $6 \times 10^{-3}$  and  $G_{II}(S)$  between  $1 \times 10^{-3}$  and  $3 \times 10^{-3}$ . These values are less than those that Brown and O'Donnell [5] reported for a polysulfone with the related structure



They obtained  $G_{ps}(X) = 0.051$  and  $G_{ps}(S) = 0.012$  employing cobalt-60  $\gamma$ -irradiation.

The NMR studies and IR studies suggest that the methyl, carbonyl, and ether groups are the parts of the macromolecule principally affected by the high-energy radiation. The higher  $G$  values for Polymer II compared to I suggest that the methylene bridge may be less stable to irradiation than the isopropylidene link in the backbone of I. The results also indicate that the structural units in I and II derived from bis(4-chlorobenzoyl)benzene impart more stability to these polymers than the  $-SO_2-$  linkage does to the polysulfone [6,7].

#### ACKNOWLEDGEMENTS

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#### REFERENCES

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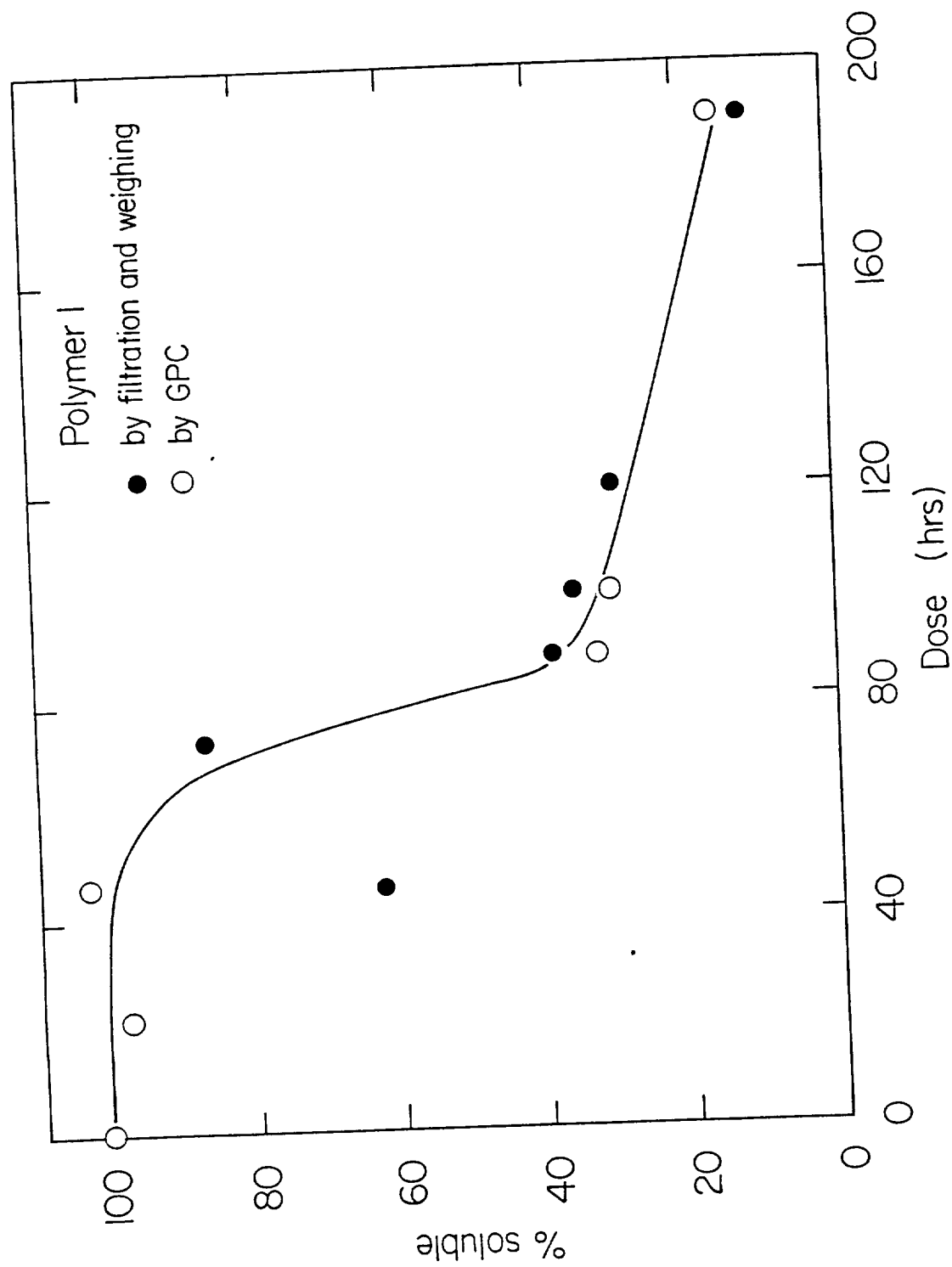


Figure 1. The percentage of the soluble component of Polymer I remaining as a function of the duration of irradiation at  $1.8 \times 10^8$  rad hr<sup>-1</sup>.

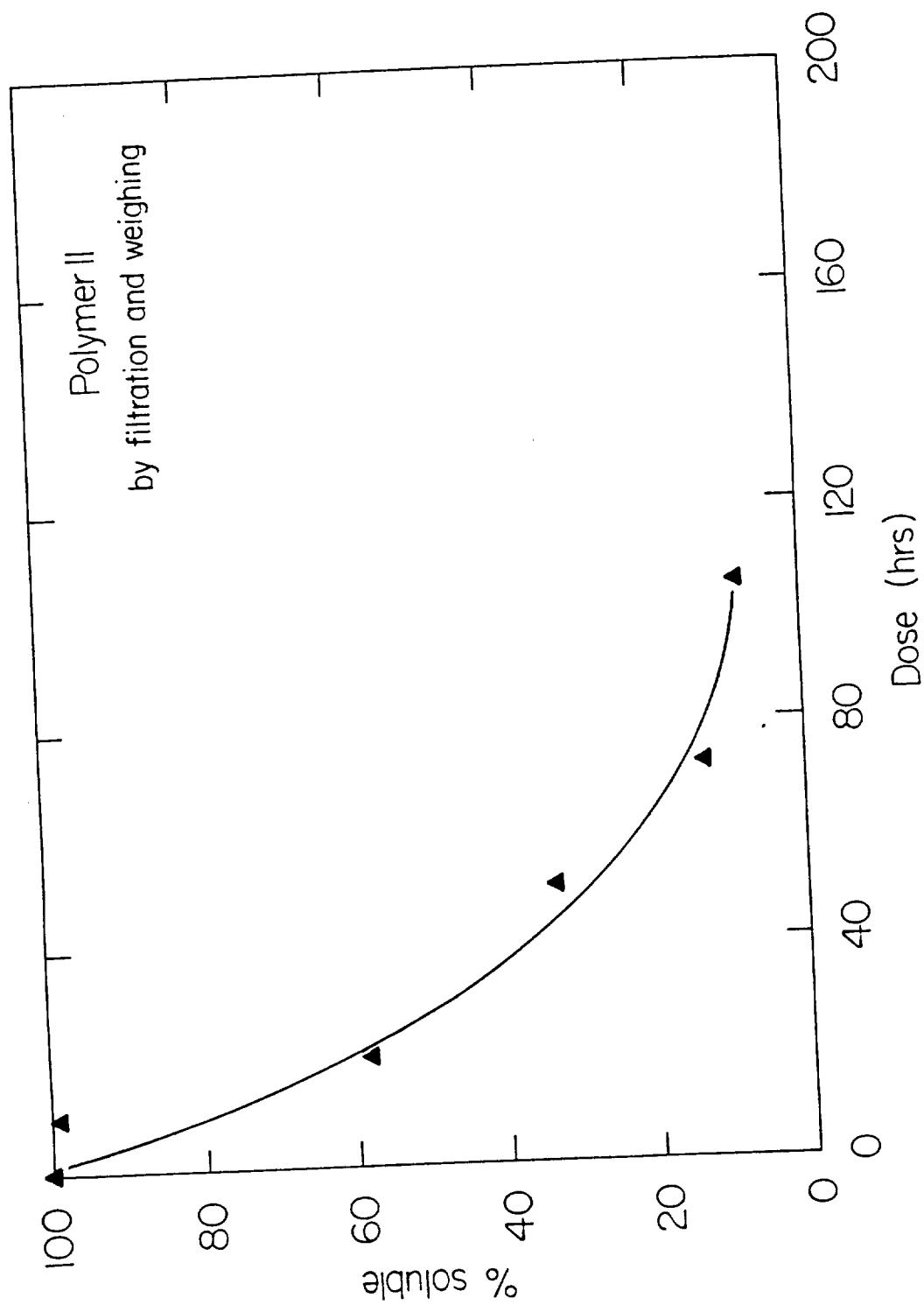


Figure 2. The percentage of the soluble component of Polymer II remaining as a function of the duration of irradiation at  $1.8 \times 10^8$  rad hr<sup>-1</sup>.

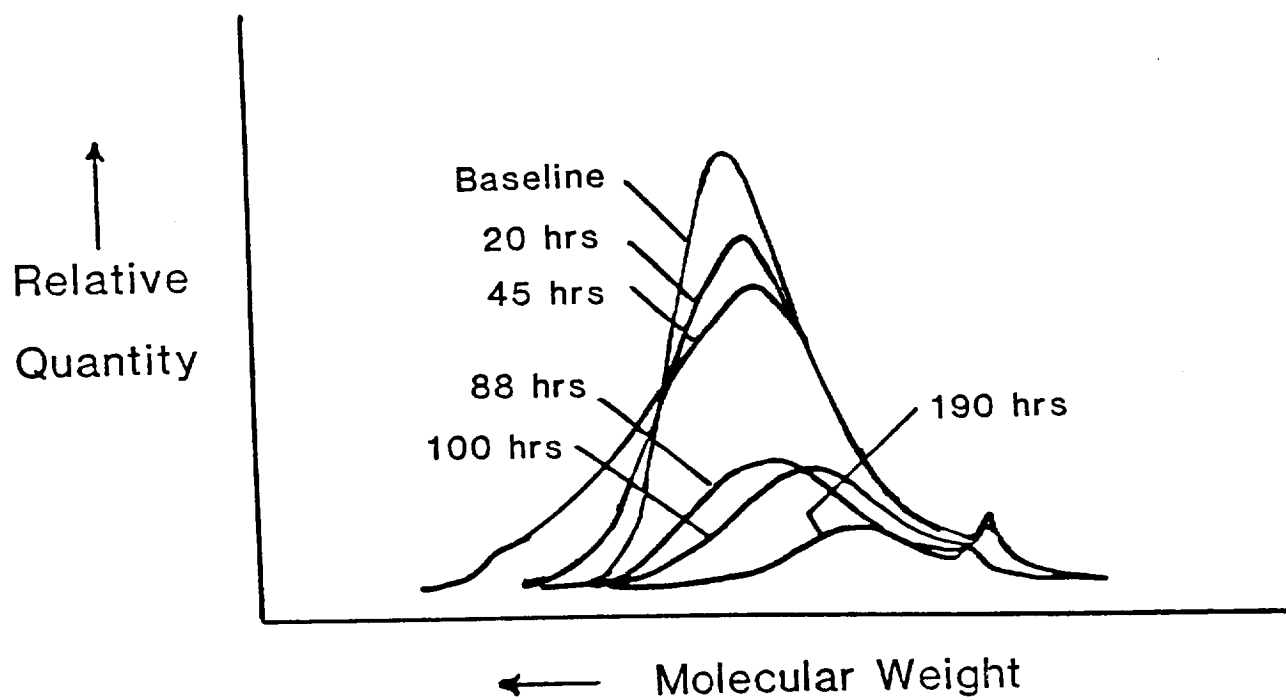


Figure 3. GPC analysis of the soluble component from films of Polymer I after different periods of irradiation.



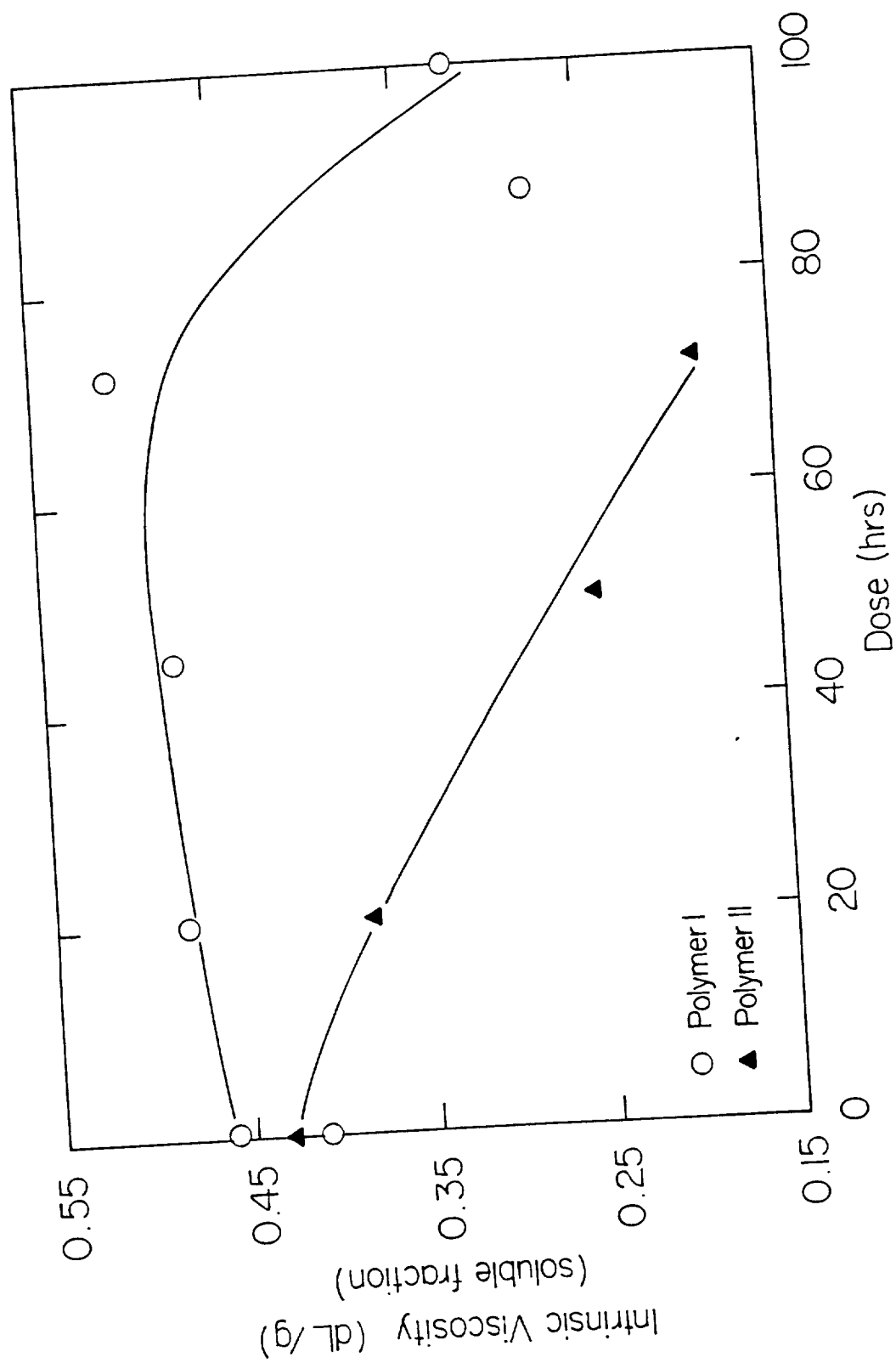


Figure 4. Intrinsic viscosities ( $\text{dl g}^{-1}$ ) of the soluble fractions in chloroform of Polymers I and II plotted as a function of the duration of irradiation at  $1.8 \times 10^5 \text{ rad hr}^{-1}$ .

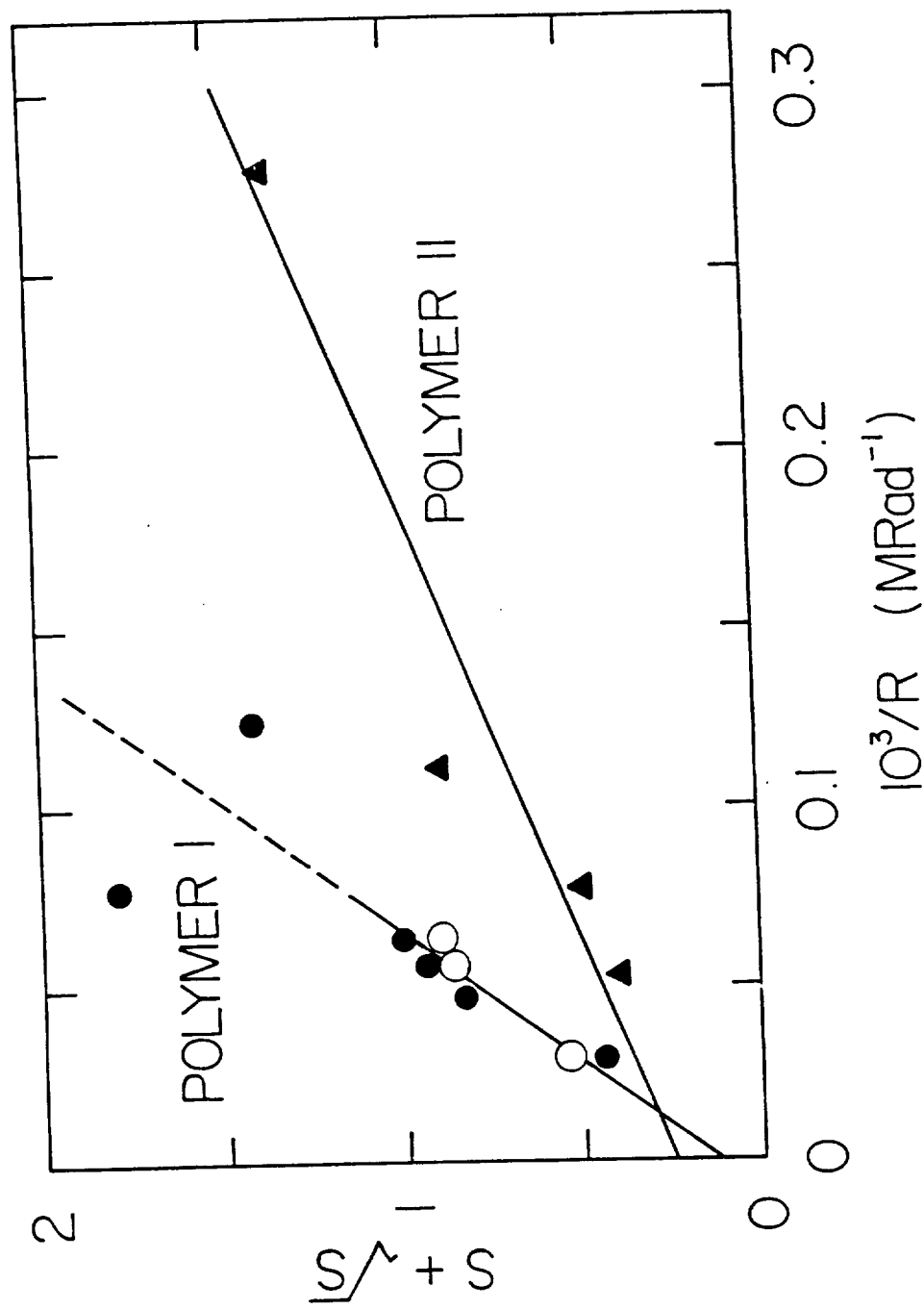


Figure 5. Charlesby-Pinner plot for Polymers I and II. Values obtained from GPC for I are plotted as open circles; those from filtration, as filled circles (Polymer I) and filled triangles (Polymer II).